Technical Report

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Recipient: FST Energy

A Cassette Based System for Hydrogen Storage and Delivery

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Executive Summary

Fossil fuels currently provide the majority of the energy which drives our society. This finite resource has several problems including sociopolitical and environmental and must be replaced in the future by sources such as wind, photovoltaic, nuclear, or biofuels. We have become accustomed to taking our energy with us primarily in the form of gasoline or diesel, and we must seek alternative methods for moving energy around. Hydrogen is a material that has the potential to substitute as a mobile energy supply for fuels such as gasoline and has some important advantages. Coupled with a fuel cell, hydrogen can produce power directly in the form of electricity without noise and without pollution. Hydrogen by weight has about three times the energy content of gasoline and a fuel cell operates approximately twice as efficiently as an internal combustion engine as found in an automobile or generator. Unfortunately, hydrogen is a gas that is expensive to liquefy or concentrate, and hydrogen must be produced using energy or energy sources in the process.

One major challenge that we address is to come up with a way to move hydrogen around in a safe, convenient, and economical manner. Hydrogen can be stored in various chemical forms and we have studied methods for managing a class of compounds called metal hydrides that hold more hydrogen than can be contained in high pressure hydrogen cylinders of the same volume or in some cases liquid hydrogen. Our strategy is based upon a cassette concept in which an easily transported, safe, inexpensive container manages the hydrogen storage material, and a complimentary unit manages the cassette

to release the hydrogen. Furthermore we intend to use the best available chemistry for our system by creating partnerships with suppliers or manufacturers. There are advantages to our cassette concept that could reduce the cost of moving hydrogen, increase the storage capacity, and increase flexibility by providing parallel operation of many small cassettes. We have demonstrated some of the concepts and are extending our studies to allow for hydrolysis reactions of the hydrides that offer a larger palate of materials from which to choose. There are opportunities and applications, particularly in the backup power market that would benefit from our system today. We are seeking to fill this need.

Goals and Status

A summary of our initial goals and the status is summarized in the table below.

Goal	***Status***
Choose Software System for Modeling	Fluent, Completed
Select Chemical Systems for Modeling	Use parameters for Sodium Aluminum Hydride in the modeling
Select Thermal Management Schemes	Identified External Heating Efficacy
Model Thermal Management Schemes	Modeled Three Schemes
Model Basic Cassette System	Completed (Excel Models
Foster Scientific Communications	See Below
Build a Team to Meet Goals	Completed, Team Members Listed Below
Presentations, Communications	See List Below
Lab Preparation and Equipment	Completed, See Below
Research Documentation Control	Continuing
Project Cost Control	Continuing
Test Reliability of Alanate	See Discussion, Terminated
Lifetime Testing	See Discussion, Terminated

In summary, we have:

- Selected parameters for a hypothetical metal hydride, using sodium alanate as a model. Applied this to several cassette system designs to meet perceived end-user requirements
- Modeled heat transfer concepts for cassette model and compared results for selected approaches
- Compared virtual cassette with other hydrogen storage methods, primarily pressure systems
- Evaluated heat transfer in selected systems
- Designed and constructed demonstration cassette system hardware and software to illustrate features of a multiplexed cassette system
- Modified materials and evaluated properties
- Compared different H2 storage systems in cassette test system
- Constructed and utilized a Sievert’s test system

- Designed and constructed cassettes to manage solid hydrides for a hydrolysis reaction
- Tested several hydrides in a hydrolysis reaction

Based upon knowledge gained during the course of our work we have expanded and refocused our studies to include several metal hydride hydrolysis systems because of the paucity of metal hydrides that have the near-term prospect of meeting the DOE gravimetric targets. It is our belief that hydrolysis of metal hydrides might have the best chance of meeting their goals at the present time, and that a safe, modular, adaptable, rechargeable and transportable system for hydrogen storage and delivery can be produced.

Accomplishments

Cassette Modeling with Fluent Modeling Software

Metal hydrides come in various flavors that may be treated thermally to release hydrogen, or may be reacted with water to release more hydrogen. Recharging expended hydrides with hydrogen releases heat or requires chemical steps and energy. Heat management of is a significant issue, because it can involve a good deal of energy, leading to energy loss when it can not be recovered and used, and/or require hardware to deal with the problem. Hardware is matter, and it takes up space, weighs something, and costs, none of which is desirable but probably inevitable. One of the goals of this work is to examine the issue of heat transfer in a cassette.

The strategy with our cassette based system is to make it simple and flexible so that it can adapt to a variety of hydrogen storage materials and applications. By keeping it simple and off loading part of the operating hardware of the cassette to a separate module, we will be able to reduce the cassette mass, volume, and cost. The cassette then becomes a more easily transported device with a minimum of hardware, allowing for the intensive heat evolution of recharging or chemical reconstitution to be handled off site. We have kept the cassette models simple and will keep this as a primary goal. A number of design elements have been produced to address specific problems.

Cassette Model Simulations

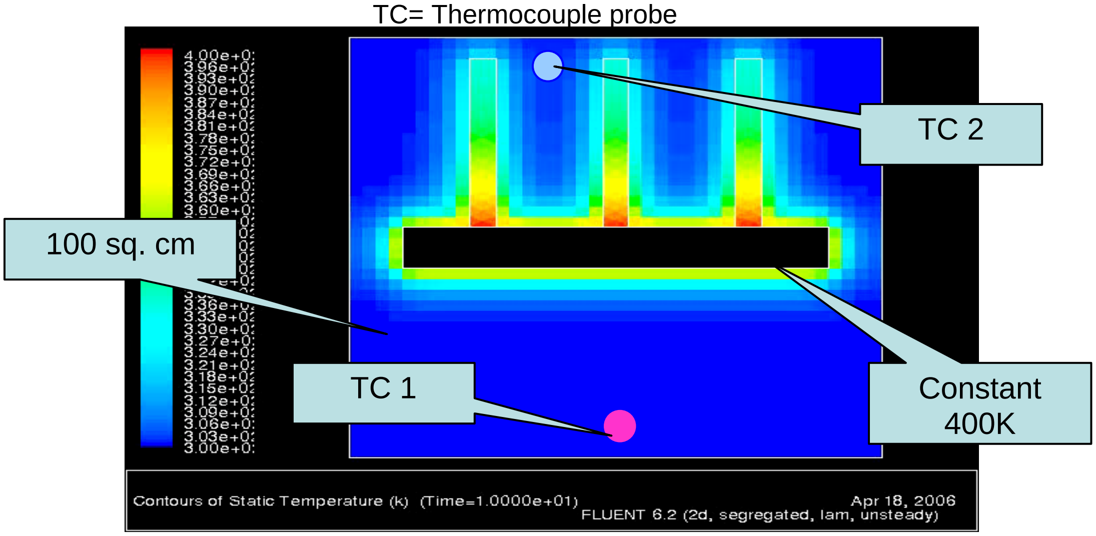
Fluent, Inc. software has been used to compare different heat transfer systems. Results for three different heating schemes illustrate the advantages of a relatively flat cassette that can be heated from the outside, keeping the cassette simple and inexpensive while simplifying heat transfer for material activation.

Figure 1 below shows the results of a heat transfer calculation on a model cassette that is 10 cm on a side (a 1 cm thick cassette would thus contain 1 liter of material).
The area in black is the constant temperature heater within the cassette. The three vertical rectangles above the heater are aluminum heat transfer fins connected to the

heater. The colors indicate the heating progress in the media, which in this case is represented by sodium aluminum hydride. The TC represent thermocouples and they will be discussed below.

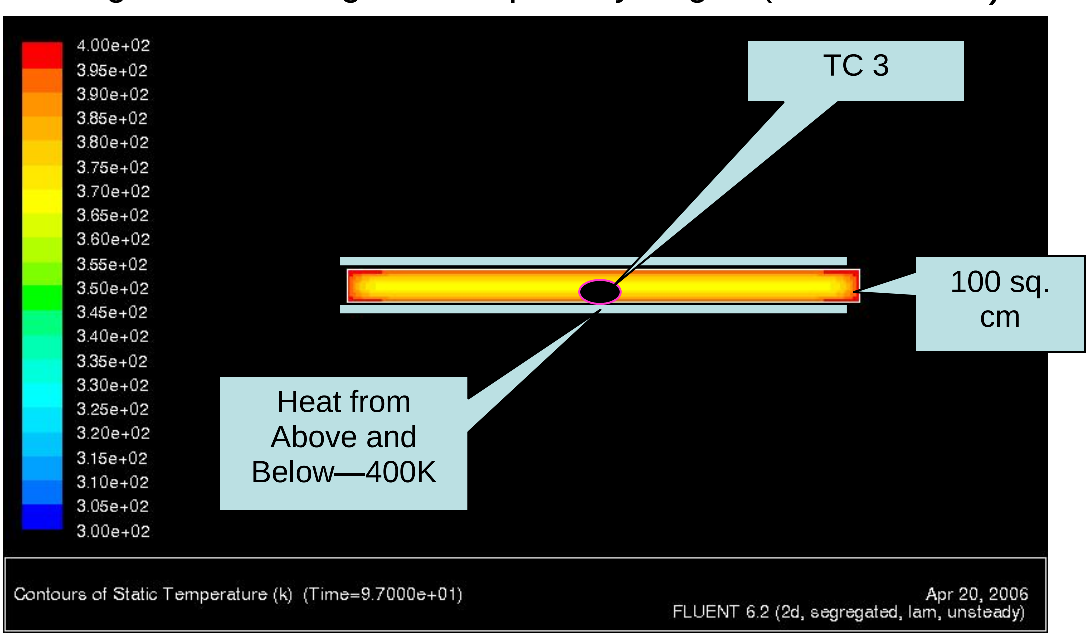
Figure 1. Heat transfer Fluent Model Illustrating Efficacy of Heat Transfer Fins (top): No Fins (bottom)

TC= Thermocouple probe



Below the heater we did not include fins so that two heating schemes—with and without fins—could be compared. We can see from this simulation that the heat transfer fins play a role in moving heat through the material but at a cost in complexity, mass, and volume. While this outcome may be obvious, it is clear that it is important to keep the heat transfer distance short. This we accomplish with a flat cassette—see Figure 2.

Figure 2. Heating Alanate plus Hydrogen (Fluent Model)

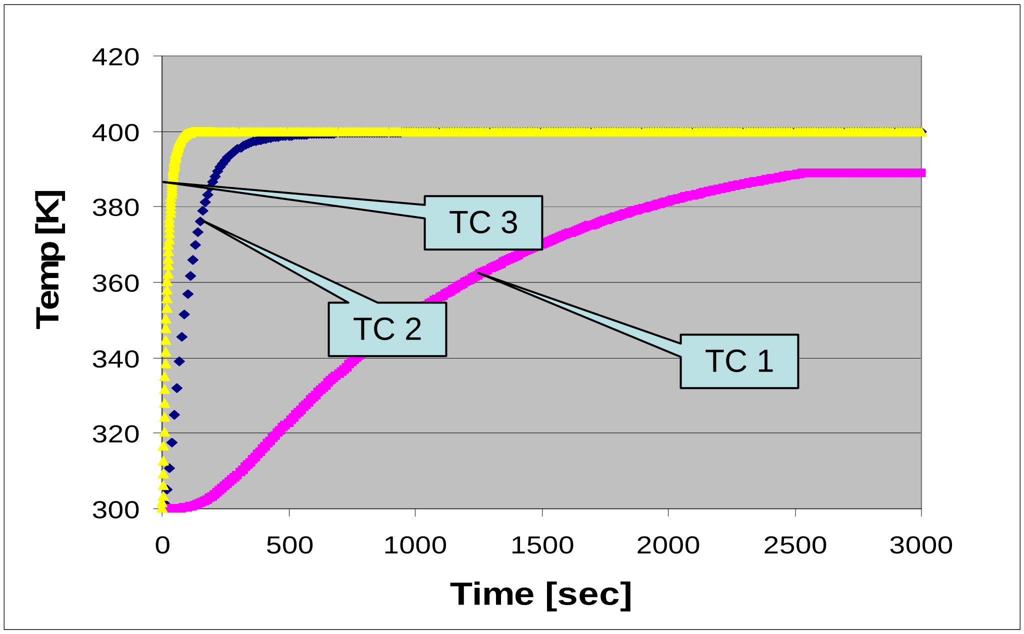


By keeping the cassette relatively thin, it is possible to heat externally without having a complex interior, keeping the cost and complexity of the cassette optimal. Since it is the cassette that is transported, refilled, marketed, and sold, this is important.

We now compare the three systems as shown in Figure 3 below. The TC represents the thermocouples with their locations shown on Figures 1 and 2, which are single volume elements in the simulation. We see in Figure 3 that the flat model with external heating achieves temperature faster than the other two models. This speaks directly to the complex UTRC cylinder hydride fuel tank that is filled with heat transfer tubes, fins and hydrogen passages. The UTRC system has the obvious advantage of rechargability through direct pressurization, but at cost of fairly complicated architecture. In spite of its complexity, it would still take some time to recharge. Whereas the flat cassette can not be recharged in place without a support structure to accommodate the internal pressure required, it can easily be refilled with charged material or recharged in a system that would provide external support to the cassette. Thus, it becomes a change out system. Changing out a cassette can be fast and relatively simple.

Data for the UTRC system, high pressure cylinders, and cassettes are compared in Table 2 and discussed further below. .

Figure 3. Comparison of Temperatures in the Previous Two Models



Comparison of Storage Systems

Excel models of several cassette systems have been developed to estimate weight and volume percentage for hydrogen storage and energy requirements for hydrogen release using prototypical and known materials. The data have been compared with conventional cylinder delivery systems (Table 1), and advanced high pressure cylinders as well as the UTRC system that was assessed by TIAX in 2005 (Table 2).

Table 1. Comparison of Cassettes with Steel Cylinder

Cassette	*4% H2*	*6% H2*	*Units*
Size	28X36X5	28X36X5	Cm
Media Wt	2.99	2.99	Kg
Thermal Mgt	0.5	0.5	Kg
Housing Wt.	1.49	1.49	Kg
Plumbing Wt.	0.25	0.25	Kg
H2 Wt.	0.12	0.18	Kg
Cylinder Eq.	0.16	0.24	Cylinders
Gasoline Eq.	0.47	0.71	Liters

Table 1 clearly illustrates the challenge of hydrogen storage, where we can deduce that a standard 2400 psi 150 lb hydrogen cylinder holds the energy equivalent of only 2.8 liters of gasoline. We show however, that a hydrogen storage cassette in a relatively small package with a 4 or 6% hydrogen weight capacity hydride is far superior in weight and volume to a cylinder—at least a factor of three in the worst case. For example, a 28X36X5 cm cassette with media that holds 6% hydrogen and a density of 0.7 is equivalent to 0.24 cylinders of hydrogen at 2400 psi. This in turn is equivalent to 0.71 liters of gasoline in energy content.

When one considers that cylinders are now used for backup power in some situations, a few small pizza box sized cassettes filled with metal hydride would facilitate refueling. More applications would certainly arise if the hydrogen storage efficiency could be improved. The story gets better when one considers that fuel cells are about twice as efficient as an internal combustion gasoline engine, they are quiet, and non polluting.

Table 2 expands upon Table 1 to include high pressure cylinders, our cassette models, and the sodium aluminum hydride storage tank system constructed by United Technologies Research Center and modeled by TIAX—DOE 2005 report.

Table 2. Comparison of Metal Hydrides with High Pressure Cylinders and Cassettes—Each System Holds 1 Kg of Hydrogen

Parameter	***Metal Hydride 1***		***Metal Hydride 2***		***Metal Hydride 3***		***5000 psi***	***10000 psi***
	%H2	***density***	***%H2***	***density***	***%H2***	***Density***		
	4	0.65	6	0.8	9	0.9		
Material Weight, kg	25		16.7		11.1		1	1
Material Volume, l	38.5		20.8		12.3		35.3	17.65
UTRC Wt, kg	58.8		39.3		26.1		14.7	15.9
UTRC Vol, l	51.7		28.0		16.6		55.3	37.6
Cassette Vol, l	42.0		24.0		13.6		55.3	37.6
Cassette Wt., kg	X		X		21.3		14.7	15.9

These data show not only the prospects for metal hydrides compared with pressurized hydrogen, the currently preferred method for most applications, but the viability of a flat cassette. In the table, the metal hydride is varied, starting with a material of 4% hydrogen capacity by weight and a density of 0.65 (the figures used by TIAX for their calculations of the UTRC model with sodium alanate) moving to future materials with higher density and hydrogen capacity. The 9% wt. capacity of hydrogen of the Hydride 3 is the DOE target for 2015. What we find at this percentage and material density of 0.9 is a cassette that is three times smaller than 10000 psi cylinders and only slightly heavier. The UTRC model tank is slightly heavier than the cassette and slightly larger, but it also includes pressurization capability and external cooling.

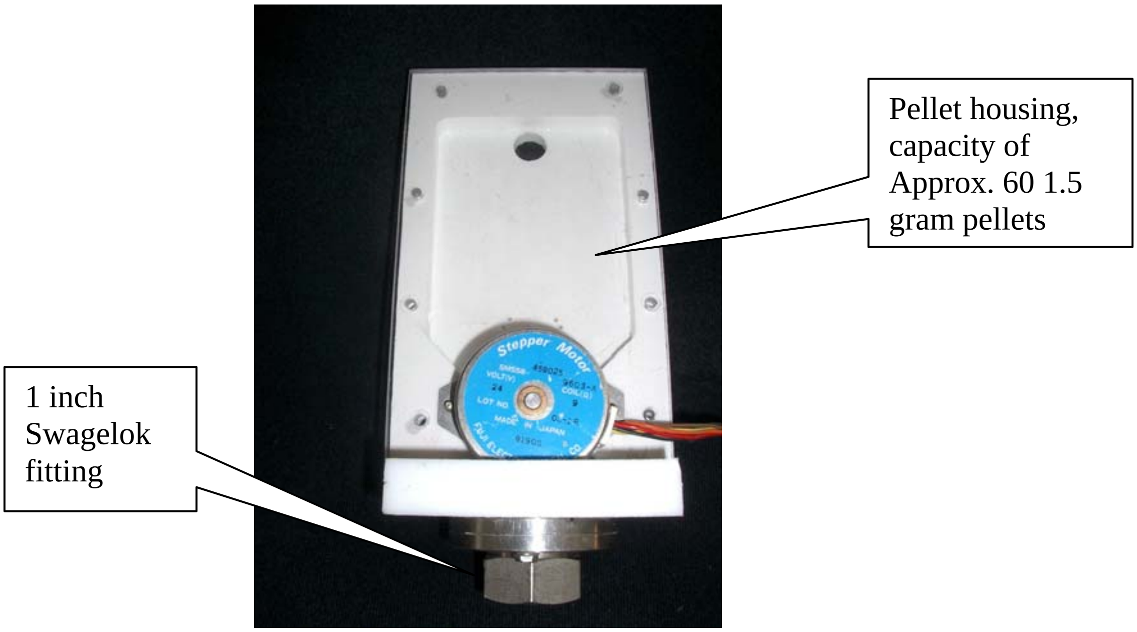
Our expectation at the beginning of this work was that three different types of materials would be evaluated in the cassette to demonstrate its adaptability. Preparations were underway to test lithium amide in collaboration with Sandia, however, the DOE dropped their interest in this material. A number of preliminary evaluations were done with sodium aluminum hydride, but this material does not have the properties that will meet the DOE goals, and this work was redirected.

Hydrolysis of Hydrides and Silicide

We initiated testing of hydride hydrolysis systems because they seem to have the best prospect of meeting the DOE gravimetric targets for 2009 and 2015. They have a number of obstacles to overcome, but the hydrogen gravimetric and volumetric hydrolysis yields based upon stoichiometry are excellent. Managing the storage material, water, by-products, and bringing the reactants together in near stoichiometric quantity with suitable kinetics are some of the challenges. Regeneration of reactant is another significant challenge.

We have developed a cassette system that delivers compressed pellets of hydrides or sodium silicide to a water reactor through a pressure and vapor interlock system. A challenge here has been to find a way to deliver the solid material to the reactor without significantly contaminating the solid reactant reservoir with water from a reaction that creates vigorous hydrogen evolution and water saturated vapor. Several prototypes have evolved to our current system, part of which is shown in Figure 4.

Figure 1. Photograph of Hydride Pellet Dispenser



Two system demonstrations were accomplished with a predecessor of the system shown in figure 4 using a material called SigNa Chem (essentially sodium silicide) that produces 9.4% hydrogen upon hydrolysis. Solids are delivered by gravity through a pressure interlock to a reactor containing water via a computer controlled system. Once a minimum desired pressure is selected in the software, the system operates to maintain this minimum pressure. As hydrogen is drawn from the system, pressure falls and more reactant is automatically added. In principle, pressure can be maintained simply by controlling the reaction rate through the addition of solid. The delivery pressure is generally set to 20 psi but pressures over 100 psi have been achieved in this reactor, and over 1400 psi in a test cell. The hydrogen yields are nearly quantitative based upon the SigNa Chem material and an excess of water. The hydrogen flow rate is typically set to ca, 12 liters per minute using a pressure regulator and metering valve, and the flow and total hydrogen production is monitored with a gas meter with a totalizing readout.

We have also looked at hydrolysis reactions of magnesium hydride and sodium aluminum hydride and mixtures of these. By mixing hydrides we have tried to achieve more favorable reaction conditions. The dispenser shown in Figure 4 was charged with 22 pellets of technical grade sodium aluminum hydride (approximately 80 % active) weighing 30.07 grams. The reactor chamber below the dispenser and interlock is charged with water and the call for hydrogen is initiated. The lower threshold pressure is set to 10 psi and the flow rate to approximately 1.5 liters per minute. The turret operated by the stepper motor picks up two pellets and drops them into the interlock region and the cassette is then isolated by closing a valve. Another valve opens and delivers the two pellets to the reactor whereupon the system pressure rises to about 25 psi. As the hydrogen flows from the pressurized reactor, pressure slowly falls to the 10 psi low pressure threshold set in the program. This initiates a call for two more pellets and the process continues. After 27 minutes, 41 liters of hydrogen have been generated and all the pellets have been consumed. Based upon 80% activity for the technical grade sodium aluminum hydride, this corresponds to 96% yield of hydrogen. This process runs totally automated initiated by a call for hydrogen.

Resistive Heating of Sodium Alanate

In addition to these diverse hydrogen storage chemistries, we also investigated modification of metal hydride properties in thermal hydrogen release reactions, in an effort to make them more amenable to the controls of our cassette system. Addition of carbon to sodium aluminum hydride to renders it electrically conductive. Preliminary experiments with ca 1 cm diameter plugs of alanate have demonstrated that these materials can be then be heated resistively. A number of challenges remain and are under investigation. These include reducing the resistance with reduced carbon loading, assess the safety of this approach, and quantitatively analyze hydrogen production with resistive heating.

Table 3. Resistance of Carbon Modified Sodium Alanate

Carbon 1 (%)	***Carbon 2*** (%)	***Al/Ni powder*** (%)	***Resistance*** (ohms)	***Thickness*** (cm)
10			7800	1
20			350	1
30			130	1
	10		>100K	1
	20		5500	1
	30		200	1
		10	>100K	1
		20	>100K	1
		30	>100K	1

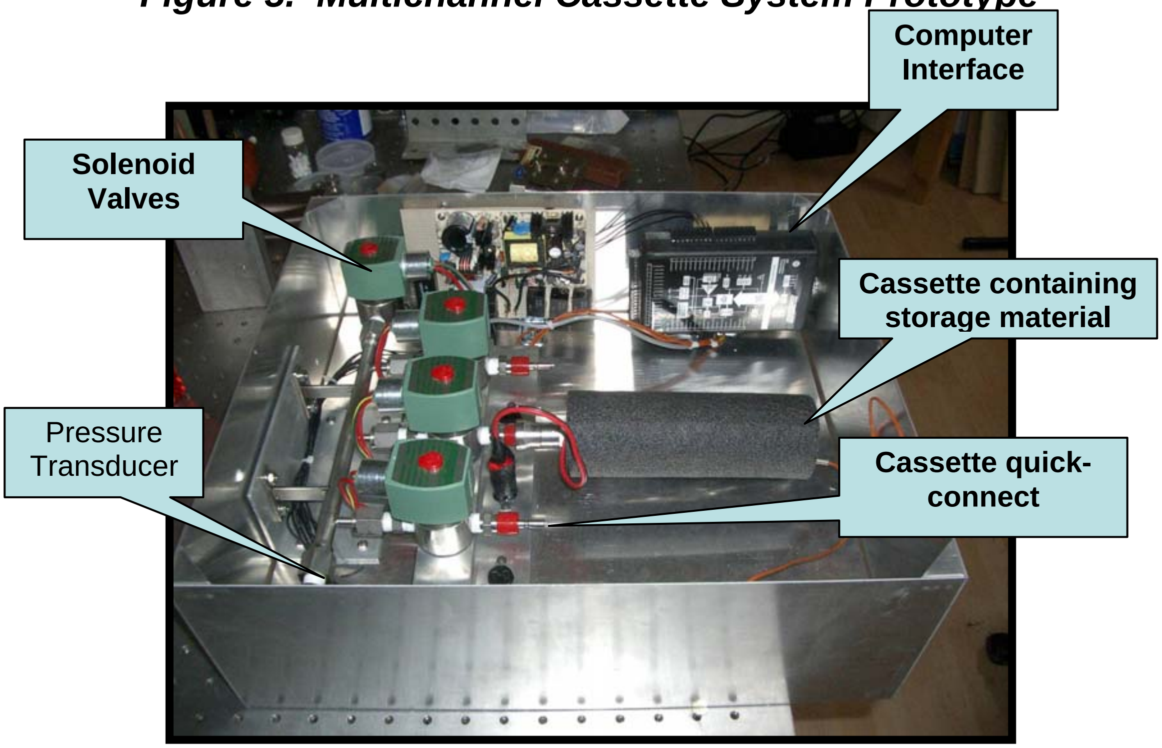
Powder Compression for Increased Density and Ease of Handling

Another modification of the hydrogen storing material is compression providing a more compact and easily handled form of these materials. We can increase the density of SigNa Chem (a form of sodium silicide) from a density of 0.7 to 2.0. We can also achieve a density of 1.2 for sodium aluminum hydride by compression. Pressures up to 50,000 lbs per sq inch have been utilized. We currently compress the material into a disk shape which has a higher density but a poorer packing density than a continuous medium. However, it is calculated that the improvement in packing density through compression is 30% or more depending upon the material.

Cassette Prototype

A laboratory test module of a three cassette system has been designed and constructed. The cassettes consist of simple tubes keeping the system simple and adaptable. These are integrated with a flexible control system that provides independent operation of each cassette, or parallel operation to meet higher demand and/or to provide a smooth transition when a cassette becomes completely or nearly completely discharged. Our implementation uses off the shelf hardware such as quick connects that have proved to be safe, easy to use, and leak free up to 1500 psi. The prototype system has the ability to evaluate three types of media systems under computer control. The system is shown in Figure 5.

Figure 5. Multichannel Cassette System Prototype

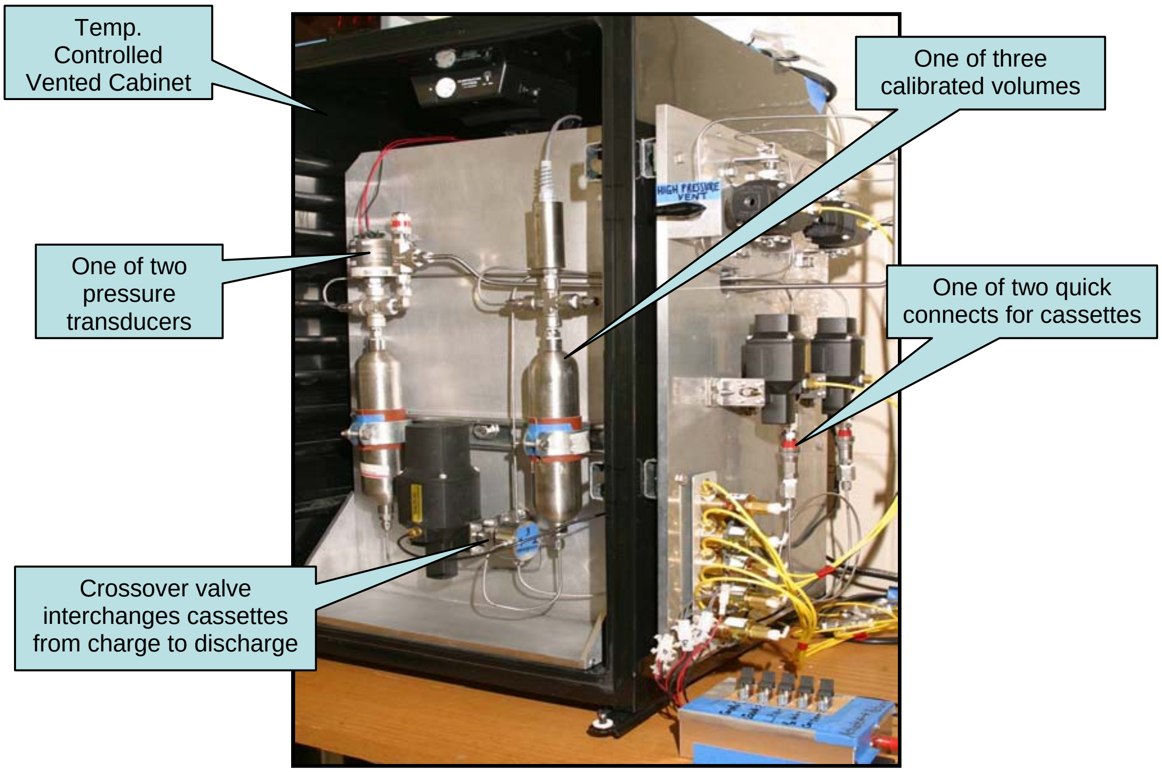


Sievert's Apparatus

A dual Sievert's test apparatus has been constructed and operates under complete computer control. This system will allow efficient life cycle testing of thermally activated materials of interest with the potential of running this cycle testing 24/7 in order to quickly reach several hundred charge/discharge cycles with a minimum of labor. This system accommodates two cassettes, each with integrated heaters and thermocouples. These plug into a gas manifold using quick connects. The hydrogen pressure is derived from a cylinder with a regulator that maintains a pressure of 1500 psi for charging cassettes. Time and temperature for charging and discharging cassettes are selected in the software with the charging of one cassette occurring while the other is discharging. Pressures and temperatures are monitored as a function of time to afford data for hydrogen uptake and release.

Figure 6. Picture of Dual Automated Sievert's

(Front cover removed for viewing)



Appendix

No finished products were developed under this award.

Publications

Presentations

- Clean Start Finalist
- DOE May 2006 Meeting, Poster
- WestStart CALSTART, June 2006 Presentation

Web site or other site that reflect the results of this project

www.fstenergy.com

Networks or collaborations fostered.

- Sandia laboratory at Livermore
- Safe Hydrogen, Andrew McClaine
- Protonics
- Altergy
- Sonoma State University, Lynn Comminsky, Chair of Physics and Astronomy,

Technologies or Techniques

Most techniques utilized are considered routine. We have developed a pellet dispensing system for hydrolysis reactions of metal hydrides and silicides. The current version of this system uses a rotor operated by a stepper motor. The rotor is notched to accommodate solid 1-2 gram pellets pressed from the metal hydride or silicide. The rotor fits at the bottom of a hopper that is filled with the pellets. Figure 4 shows a photograph of this device. Below the rotor is an interlock system that delivers pellets by gravity to a reactor containing water, at the same time preventing pressure and water vapor from reaching the hopper and contaminating the hydride. Upon command from a computer program, the rotor picks up a pellet and delivers it to the interlock system that then delivers it to the reactor. The chemical reaction produces hydrogen pressure in the reactor, which flows from the reactor at a preset rate to metering hardware. The reactor minimum pressure is set in the software and whenever hydrogen pressure falls below this threshold, another cycle is initiated. We have run this system in earlier incarnations at up to 1 standard cubic foot of hydrogen per minute. The later versions typically run at about 10 liters per minute, or about that required for a 5 KW fuel cell. An example of a 1.5 liter per minute run is discussed above.

Other products such as data bases, software

Software to run Sievert's, Prototype, and Solid Reactor System described in the narrative.

Software was developed to operate the Data Translation 9806 USB hardware via their DT Foundry program. This system operates the Sievert's apparatus via monitoring temperature and pressure and controlling valves for the system operation. It can be set to conduct charge and discharge cycles through the analog input and digital I/O system.

Software was developed to monitor temperature and pressure on the prototype cassette system discussed above. The software monitors pressure in the manifold, temperature in the three cassettes, and the control valves on the manifold and each cassette.

Software was developed to operate the hydrolysis reactors. This monitors temperature and pressure and controls the valves and stepper motor system.

For Projects involving computer modeling

Model description

The models described in the narrative above utilized Fluent, Inc. software:

Fluent Computational Fluid Dynamics 6.2.16
Flow Wizard 2.0.4
Gambit 2.2.30
Exceed 10.0 XServer

These are described at www.fluent.com

Performance criteria for the model related to the intended use

Three models were compared to evaluate heat requirements for each system. No criteria were set.

Test results of the model, sensitivity analysis… as appropriate

Sensitivity analysis was not systematically conducted in this work. The purpose was to compare three basic heat transfer concepts as discussed above under equivalent conditions.

Theory behind the model, non technical

The systems are finite difference models for simulation of heat flow, whereby the physical hardware is modeled by constructing a computer aided design. The design is then divided into a number of small volume elements with specific properties so as to represent the hardware. Initial boundary conditions are then set, such as temperature, pressure, flow rate, and properties of materials, etc. Energy is then introduced into the system in a specified way and the effect on each volume element is calculated for each iteration using appropriate energy equations. The calculations continue to a specific point or time. The process evolution may be depicted in a video or via graphs.

Mathematics to be used, including formulas

This is covered to some extent in Fluent documentation and on their website at www.fluent.com

Whether the theory or math algorithms were peer reviewed

This is commercial software and not peer reviewed.

Hardware requirements

The hardware that is modeled is discussed in the narrative above.

Documentation, users guide, model code

This is commercial software and documented by the manufacturer.